Biodiesel production using 4-dodecylbenzenesulfonic acid as catalyst

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ABSTRACT

The synthesis of biodiesel from triglycerides and methanol using 4-dodecylbenzenesulfonic acid as catalyst was studied. The use of acid catalysts in the production of biodiesel has the advantage that in addition to accelerating the transesterification of triglycerides, they also catalyze the esterification of free fatty acids and, moreover, they do not form soaps or emulsions. Regarding the 4-dodecylbenzenesulfonic acid catalyst used in this work, it has a further advantage in that it has a hydrophobic moiety in its molecular structure, which permits a much higher transesterification rate than that of other acid catalysts and, hence, conversions higher than 95% can be attained under mild reaction conditions in less than 3 h.

From the results of a first set of experiments, an empirical model was calculated that related the values of conversion, at 3 h of reaction, and the values of the influencing factors quantitatively. From this model, it was found that the effects of temperature and the catalyst/oil molar ratio meant that the higher the values of any of these factors, the higher the conversions obtained. Conversely, methanol proved to be an obstacle at low conversions because it slowed down the reaction. However, under high temperature and/or high proportions of catalyst, (i.e., for conversions >80%), higher proportions of methanol also favored higher conversions.

A second set of experiments was also carried out at 80 and 90 °C and from the joint analysis of the results of all experiments performed in this work (first and second sets) it was observed that the transesterification kinetics reflected a first-order reaction, with an activation energy of 66.3 kJ/mol. At 90 °C it was possible to obtain conversions higher than 98% in less than 2 h.

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1. Introduction

The substitution of traditional sources of energy such as coal, oil or natural gas by renewable energies is driven by a variety of reasons that may be of the economic and/or environmental type or may even be due to the diversification strategies of the geographic origin of energy suppliers. Among renewable energy sources, biodiesel is becoming increasingly more important owing to the simplicity of the technologies involved in its production process. This biofuel is mainly obtained by the transesterification of triglycerides with an excess of a short-chain alcohol, usually methanol, in the presence of a basic homogeneous catalyst such as potassium or sodium hydroxide. The main advantage of using a basic catalyst is that it allows very fast transesterification reactions but the main disadvantage is that this type of catalyst requires the use of high-purity oils or fats, owing to two main problems when water and/or free fatty acids (FFAs) contaminate the raw material: first, the presence of water

in the oil leads to the hydrolysis of the biodiesel formed and, second, FFAs form sodium salts (soaps) in the reaction medium, which generates emulsions and hinders the settling of the glycerol in the reaction mixture and hence its separation from the biodiesel [1,2]. In fact, in order for basic catalysts to have adequate performance, the FFAs proportion must not exceed 0.5% (w/w) and the water content must be less than 0.3%. Even so, the process is still not completely free of difficulties. This requirement of using high-quality raw materials in the base-catalyzed process implies high production costs and, as a result, means that the biodiesel thus obtained is not economically competitive with petrodiesel.

However, the global cost of the biodiesel production process could be decreased if low-priced raw materials, such as waste cooking oils or inedible oils and fats, could be used [3–8]. The problem that arises when trying to use this type of oil/fat is that they often contain high proportions of FFAs and, consequently, their transesterification cannot be carried out with alkali metal hydroxides in a single-step process. In these cases, the most appropriate catalyst seems to be one of the acid type because an acid catalyst can simultaneously speed up both reactions: the esterification of fatty acids and the transesterification of triglycerides.

Some mineral acids (inorganic), such as sulfuric, phosphoric or hydrochloric acid, have been tested in transesterification reactions and it was found that with this type of catalyst there were no problems deriving from soap formation or phase separation due to the formation of emulsions, although the shortcoming was that the kinetics of the transesterification process was much slower (about 4000 times) than in the process catalyzed by a basic catalyst [9–11]. The slow reaction rate with inorganic acid catalysts seems to be due to the fact that in this case the reaction occurs in the alcoholic phase and in this phase the concentration of oil is very low due to the low solubility of the oil in the alcohol. This means that the global reaction rate is controlled by the rate of mass transfer between the oily and alcoholic phases.

In light of the foregoing and in view of the slow reaction rate they were able to provide, these acid catalysts were eventually discarded as being suitable and several alternative methods were proposed to solve the problems caused by the presence of FFAs [12]:

(a) The initial transformation of FFAs into soaps and the removal of these by washing with water.
(b) The addition of an excess of catalyst with respect to the amount of FFAs.
(c) Extraction of the FFAs with a selective solvent.
(d) Distillation of the FFAs.
(e) FFAs preesterification with an acid catalysis, followed by transesterification with a basic catalyst.
(f) The use of Brönsted acids at high temperature to catalyze the esterification and transesterification reactions.

Nevertheless, none of these alternative procedures solved the problem definitively since all of them entailed additional costs because they increased the number of steps of the overall process or required more expensive operating conditions.

There is, however, another alternative route that has not been sufficiently explored, namely the use of organic acids of the alkyl-benzenesulfonic type as catalysts [13]. In this case, an aromatic ring linked to an alkyl chain endows the acid with a lipophilic nature, making it at least partially miscible with the oily phase, and consequently this oily phase is where the transesterification reaction mostly occurs. In this case, since the solubility of the alcohol in the oily phase is significantly higher than that of triglyceride in the alcoholic phase, the reaction rate is much faster than in the case of inorganic acid catalysts. Accordingly, alkylbenzenesulfonic-type catalysts prevent, or at least reduce, the drawbacks of inorganic acid catalysts, such as their slow kinetics or corrosion of the equipment. This type of catalyst has mainly been studied in solid form as cation-exchange resins or as ordered mesoporous silica (SBA-15) containing sulfonic acid groups [1,14,15]. However, regarding the kinetics of the reaction, for two main reasons all solid catalysts have disadvantages with respect to liquid catalysts. First, all solid catalysts usually have a lower number of functional groups per unit of catalyst volume or mass than those of a liquid catalyst. The second drawback stems from the slow diffusion of the reactants into the solid pores, a circumstance that is exacerbated in a case such as this due to the viscosity of the oily reactants participating in the reaction. These two aspects lead to slower kinetics than that obtained with a liquid catalyst.

Since these problems do not occur if the catalyst is liquid, in the present work we were prompted to study the behavior of a homogeneous acid organocatalyst in the synthesis of biodiesel through the transesterification of triglycerides with methanol; specifically, an alkylbenzenesulfonic acid (4-dodecylbenzenesulfonic acid (DBSA)), which can be used with low-priced raw materials and which achieves very high conversions in a reasonably short reaction time. Additionally, this catalyst is a low-cost commercial product and is therefore easily accessible. Unlike what happens with

inorganic acid catalysts, with this catalyst it is not necessary to add large proportions of alcohol; only proportions equal to or lower than those used in the case of a basic catalyst are needed. Neither are high temperatures required (>100 °C), unlike the case of solid catalysts.

There is only one slight disadvantage in using this liquid catalyst with respect to the basic catalyst: slightly higher temperatures are required to complete the reaction in a short time. However, this problem is offset by the significant advantages of this liquid catalyst: low-cost oils or fats can be used and there is no generation of soaps or emulsions.

Accordingly, a biodiesel preparation process that uses the DBSA catalyst seems to be viable and at the same time competitive with current processes that employ basic catalysts. With this in mind, the main objective of this work was to study the influence of the transesterification conditions on the reaction kinetics, by analysis of the effect of three factors (temperature, the catalyst/oil molar ratio and the methanol/oil molar ratio), on the conversion of triglycerides at certain reaction times. We also addressed the optimization of the values of these factors. To achieve this goal, response surface methodology was used.

2. Experimental

2.1. Materials

Refined sunflower seed oil (Sovena, Spain), and methanol (>99.8%, Scharlau, Spain) were used as reactants for the transesterification experiments. Oleic acid (>97%, Fluka, Belgium) was the fatty acid used to study the effect of the FFAs on the kinetics of the transesterification reaction. The catalyst was DBSA (mixture of isomers, ≥95%, Sigma-Aldrich, Spain). Concentrated sulfuric acid (95–97%), supplied by Scharlau (Barcelona, Spain), was also used as a catalyst in a test experiment to compare its catalytic activity with that of DBSA. Deuterated chloroform (CDCl$_3$, 99.8% D, Sigma-Aldrich, Spain) was used as a solvent in the ^{1}H NMR analysis of the reaction mixture. All reagents were used as received, without further purification.

2.2. Procedure for the synthesis of biodiesel

Biodiesel was prepared using the triglyceride transesterification reaction with methanol, with DBSA as the catalyst. The operating conditions in each of the experiments are shown in Table 1. For each experiment, the preset proportions of oil and catalyst were mixed in a 50-mL reactor (a glass Erlenmeyer flask with a screw cap), which was immersed in a thermostatic bath so that the oil and the catalyst would reach the preset operation temperature. Then, the required amount of methanol was added to the reactor. The reactant mixture was stirred at 400 rpm using a Teflon-coated magnetic stir-bar. The progress of the reaction was measured at different reaction times by analyzing (^{1}H NMR) the amount of triglycerides remaining in the reaction mixture. To prevent methanol loss due to evaporation in each sampling, each type of experiment was replicated a number of times equal to the number of samples taken for their analysis; that is, the reaction was carried out in three to six reactors for each set of experimental conditions, and the composition of the reaction mixture in each reactor was analyzed at a different time.

2.3. Analysis of biodiesel by ^{1}H NMR

Different experimental techniques have been used to monitor the progress of the conversion of triglycerides in the reactions involved in biodiesel production; gas chromatography (GC) is probably the technique most widely used. However, the proton nuclear magnetic resonance spectroscopy (^{1}H NMR) technique has been

Table 1
Experimental design matrix (Design I): levels of the factors and values of the responses.

Experiments		Factor levels						Response values		
		Temperature		Catalyst/oil		Methanol/oil		Conversion 1 h (%)	Conversion 3 h (%)	Conversion 6 h (%)
Standard order	Run order	Real values (°C)	Coded values	Real values (molar ratio)	Coded values	Real values (molar ratio)	Coded values			
1	2	64	−1	0.03	−1	3	−1	18.6	50.9	77.1
2	5	76	1	0.03	−1	3	−1	39.8	71.2	89.9
3	4	64	−1	0.09	1	3	−1	48.9	88.7	92.4
4	13	76	1	0.09	1	3	−1	77.7	90.0	92.7
5	9	64	−1	0.03	−1	9	1	6.4	19.8	46.8
6	11	76	1	0.03	−1	9	1	15.6	58.4	86.1
7	10	64	−1	0.09	1	9	1	22.0	71.0	93.5
8	12	76	1	0.09	1	9	1	67.8	95.4	99.1
9	3	70	0	0.06	0	6	0	47.1	81.3	96.4
10	8	70	0	0.06	0	6	0	41.6	80.8	96.0
11	1	70	0	0.06	0	6	0	38.9	83.4	95.6
12	7	70	0	0.06	0	6	0	35.2	80.5	96.6
13	6	70	0	0.06	0	6	0	39.8	83.4	96.3
14	16	59.9	−1.68	0.06	0	6	0	23.3	60.6	86.0
15	15	80.1	1.68	0.06	0	6	0	70.8	95.8	98.3
16	14	70	0	0.01	−1.68	6	0	1.5	5.9	20.3
17	19	70	0	0.11	1.68	6	0	65.3	96.0	>99.5
18	17	70	0	0.06	0	1	−1.68	33.0	46.0	51.0
19	18	70	0	0.06	0	11	1.68	24.1	77.2	95.7

used previously [16–18] and was the method employed here because this technique is faster and easier than other analytical methods. Although we have not found comparative studies between GC and ^{1}H NMR methods for the transesterification reaction in the literature, there is at least one work that makes this comparison for the determination of fatty acids and fatty acid methyl esters, the authors concluding that the results obtained using both techniques are in good agreement [19]. Thus, since triglycerides, biodiesel and fatty acids are highly related compounds, it seems reasonable to assume that the same conclusion would be valid for the transesterification process. Despite, in this work, we have also checked the agreement (Section S4 in the Supplementary content) between the results from both types of analysis in the case of the final biodiesel and we have found that by using ^{1}H NMR fully reliable results are obtained.

To obtain the ^{1}H NMR spectrum, about 0.02 g of sample was added to 0.6–0.7 mL of deuterated chloroform, with tetramethylsilane (TMS) as internal standard, contained in a RMN 5-mm tube. Spectra (24 scans) were obtained using a Varian Mercury 200 MHz NMR spectrometer at 298 K. Fig. 1 shows the evolution of the spectra, ranging from that of the sunflower oil used in this case as the raw material in Fig. 1a, to the spectrum of biodiesel, Fig. 1c, and to an intermediate spectrum of partially converted oil, Fig. 1b.

The relevant signals chosen for integration were those of the methylene groups in the glyceride part of the triglycerides at 4.07–4.35 ppm (4H) and those of the methoxy groups in the methyl esters (biodiesel) at 3.67 ppm (3H). However, this procedure is not straightforward because monoglyceride and diglycerides signals overlap with the right half of the set of triglyceride signals i.e., with the signals between 4.07 and 4.22 ppm, according to our measurements [20]. With this in mind, to determine the conversion of triglycerides, only the area of the peaks between 4.22 and 4.35 ppm (the area of the left half of the peaks of the triglycerides) was measured and this value was multiplied by two. Thus, our measurements correspond only to triglycerides. The difference between the peak areas from 4.22 to 4.35 ppm and the peak areas from 4.07 to 4.22 ppm, is the area corresponding to mono- and diglycerides. This difference is small in the course of the reaction, which means that mono- and diglycerides are present in small proportions. When there was no signal from 4.07 to 4.35 ppm at the preset reaction time, it was assumed that there was no type of glyceride present.

We also verified this by CG–MS (see Supplementary content, Section S4)

The major differences between the ^{1}H NMR spectra of the sunflower oil, Fig. 1a, and the resulting fatty acid methyl ester, Fig. 1c, lie in the disappearance of the signal from the glyceride protons at 4.07–4.35 ppm and the appearance of a signal from the protons of the methyl group of the ester at 3.67 ppm.

Then, the conversion of triglycerides $X(\%)$ to biodiesel was calculated using Eq. (1), from the integration of the peaks of the glyceride, I_{TG}, and of the methyl ester protons, I_{ME}, [18]:

$$X(\%) = \frac{4 \times I_{ME}}{4 \times I_{ME} + 9 \times I_{TG}} \times 100 \qquad (1)$$

In Eq. (1), the factor of four is due to the four hydrogen atoms in the two C—H bonds present in each of the two methylene groups of the glyceride part of each triglyceride molecule, and factor nine comes from the hydrogen atoms in the three C—H bonds existing in each of the three methoxy groups resulting from the transesterification of each triglyceride molecule.

2.4. Design of experiments

The aim of this research was to determine the quantitative influence of the operating conditions (factors) on the conversion (response) of the transesterification reaction of triglycerides with methanol using an acid organocatalyst, with a view to obtaining useful information for later economic optimization of the global process. Consequently, the research reported here was first planned through a factorial design of experiments as an initial tool to achieve the objectives of this work because of its usefulness in determining the existence of cause-effect relationships [21,22].

2.4.1. Response and factors identification

The conversion, at a specified reaction time, was selected as the response variable. In the present work this variable is represented by an X. The measurement of this parameter was carried out using ^{1}H NMR spectroscopy, as described in Section 2.3.

The factors that may influence the conversion and the kinetics of the transesterification reaction are well known: moisture, the FFAs content, the catalyst/oil molar ratio, the methanol/oil molar ratio, temperature, and the stirring speed [23–30]. The factors whose
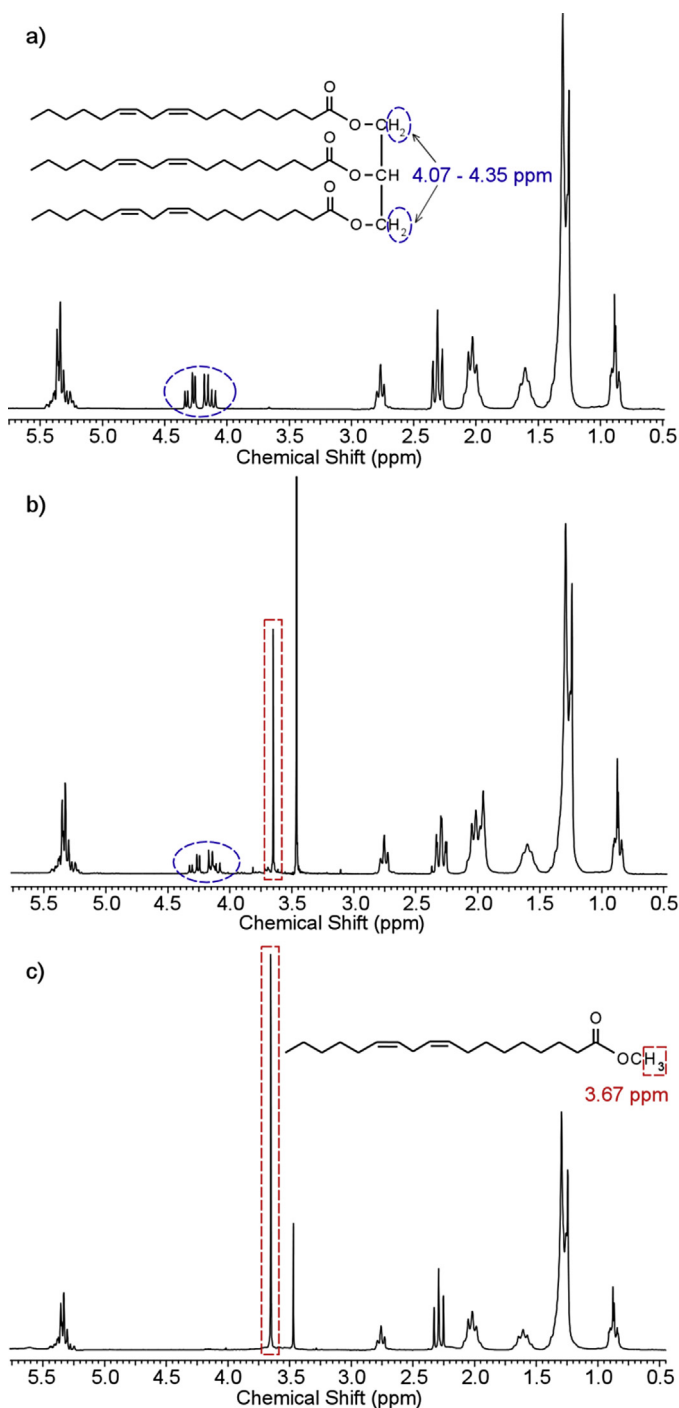
Fig. 1. Evolution of the ^{1}H NMR spectra in a transesterification reaction according to the progress of the reaction: (a) oil (triglycerides); (b) spectrum of the reaction mixture with partially converted triglycerides; (c) full conversion of triglycerides.

influence on the conversion was studied here were temperature (T), the catalyst/oil molar ratio (Cat) and the methanol/oil molar ratio (Met). The stirring rate was kept constant at 400 rpm because the stirring rate itself is only of importance during the first moments of the reaction, when it is desired to prevent the global kinetics being controlled by mass transfer phenomena due to the existence of two immiscible phases [24]. Once a certain amount of product has appeared in the reaction mixture, the miscibility of the reactants increases markedly, such that control of the global kinetics by mass transfer disappears. The influence of water and FFAs was also studied via specific experiments.

2.4.2. Identification of the levels of the factors

The T factor values selected, in a first set of experiments, were 64 °C as the low level and 76 °C as the high level of the experimental design. This range of values was used in an attempt not to surpass the boiling point of methanol too much in order to prevent excessive pressure in the glass reactor. This range of values of the T factor is higher than that used with basic catalysts, but the difference is not very large and the higher temperatures facilitate the separation of the methanol once the reaction has finished.

With respect to the catalyst, the low level of the experimental design selected for the Cat factor was 0.03:1 and the high value was 0.09:1. Once the range of values of the T factor had been fixed, the values selected for the Cat factor were as low as possible, attempting to minimize costs but also with a view to reaching a triglyceride conversion >95% over a wide range of reaction times in order to gather sufficient experimental data to determine the influence of the Cat and T factors on the reaction kinetics.

Finally, the selected values of the Met factor were 3:1 and 9:1 as low and high values of the experimental design, respectively. These values are similar to those used in a previous work with acid organocatalysts [13] with a more complicated molecular structure than that of the catalyst used in this work. However, these values are very low in comparison with the proportions used in other works using homogeneous or heterogeneous inorganic acid catalysts, in which values of the Met factor higher than 30:1 are very common [2,24]. The reason for these differences in the methanol proportions has already been outlined briefly in the introduction section of this work. In the case of a mineral acid catalyst, the transesterification reaction occurs in the alcoholic phase and, since the solubility of the oil in alcohol is very low, the result is a decrease in the reaction rate. This decrease is due to two reasons: (1) a high proportion of the oil present in the reactor is not readily available for reaction, and (2) a mass transfer step from the oil to the alcoholic phase is necessary. In this scenario, the best option for increasing the reaction rate is to raise the amount of oil in the alcohol phase by using very high alcohol/oil molar ratios. By contrast, with the acid organocatalyst used here, the reaction takes place in the oily phase, or at least in the interphase. In this case, since the solubility of the alcohol in the oil is higher than the inverse, both reactants have greater availability and the reaction rate can be faster than in the former case. The main problem of using high Met values, besides the increase in costs due to the manipulation and loss of reactant, is the increase in the overall cost of the process, since separation of the biodiesel and glycerol phases becomes more difficult in the presence of high amounts of alcohol because alcohol favors glycerol-biodiesel miscibility [23,24]. In any case, because the presence of an excess of alcohol is, in principle, necessary to displace the equilibrium reaction toward biodiesel formation in order to reach high conversions, in this study the low level of the Met factor was the stoichiometric proportion, 3:1, and the high level three-fold higher, 9:1, in an attempt to cover a wide range of Met values.

To facilitate interpretation of the results and to compare the influence of the factors objectively, all these real values of the factors were encoded by assigning a value of −1 to the low level of each factor, and a value of +1 to the high value. The coded values were calculated from the real values of the factors by using Eq. (2):

$$x_i = \frac{\xi_i - \xi_{i,\text{center}}}{\xi_{i,\text{max}} - \xi_{i,\text{center}}} \qquad (2)$$

where x_i are the coded values, and ξ_i, $\xi_{i,\text{center}}$ and $\xi_{i,\text{max}}$ are the real, the center real, and the maximum real values of the range studied for the i factor, respectively. The real and coded values are given in Table 1.

Table 2
Operation conditions of the Design II experimental plan and values of the responses.

| Experiment	Factor levels (real values)			Response values at several reaction times (%)						
Number	T (°C)	Cat	Met	$X_{0.5\,h}$	$X_{1\,h}$	$X_{1.5\,h}$	$X_{2\,h}$	$X_{3\,h}$	$X_{4\,h}$	$X_{6\,h}$
1	80	0.03	4	18.8	44.6		74.9	86.5	92.2	94.2
2	80	0.03	6	15.7	39.0		71.9	n.d.[a]	90.8	97.6
3	80	0.03	9	8.0	26.5		63.9	74.9	80.1	94.7
4	80	0.06	4	45.4	75.5		94.6	97.0	98.9	>99.5
5	80	0.06	6	38.3	73.5		91.0	95.8	96.4	>99.5
6	80	0.06	9	31.2	64.9		88.2	96.7	98.0	>99.5
7	80	0.09	4	68.7	88.3		97.4	99.1	99.1	>99.5
8	80	0.09	6	63.4	82.3		98.3	>99.5	>99.5	>99.5
9	80	0.09	9	45.5	n.d.[a]		94.4	>99.5	>99.5	>99.5
10	90	0.03	4	36.7	67.4	80.4	85.7	92.6	97.3	
11	90	0.03	6	36.4	63.1	75.1	86.2	91.3	97.0	
12	90	0.06	4	66.4	88.5	97.5	98.9	99.3	>99.5	
13	90	0.06	6	66.2	89.6	94.6	98	>99.5	>99.5	

[a] No data.

2.4.3. Selection of the experimental design

The research was initially planned as a 2^3 full factorial design of experiments with eight experiments in order to determine the three main effects and the two-factor and three-factor interactions on the conversion of triglycerides at different reaction times. To check the existence of curvature in the effects, five more experiments in the central point of the experimental design were added.

Once the ANOVA had been applied to the results it was found that the effect of the curvature was significant, implying that a linear model was not adequate for describing the quantitative relationship between the values of the factors and the values of the response. This result is not new and several authors who have applied the response surface methodology previously for the study of oil transesterification reactions for biodiesel synthesis have obtained second-order models as a result [5,31–34]. Accordingly, the range of values of the factors studied was broadened by adding axial points such that, finally, the factorial design became a central composite design, designated Design I. It consisted of a 2^3 full factorial design (eight experiments in the factorial points) extended with five replicates of the center point, plus six experiments at the axial points, with a total of 19 experiments. The distance from the center point to the axial points (α) was selected for a rotatable design, where α is the number of factorial experiments raised to the power of $1/4$ ($\alpha = \pm(8)^{1/4} = \pm 1.68$). The design matrix, given in Table 1, lists the real and coded values of the synthesis conditions in each experiment in the standard order and also in the randomized order (run order) – the order in which the experiments were performed – to avoid biased results [22].

In view of the results obtained in the experiments included in Design I, it was decided to expand the experimental region further in an attempt to reach higher conversions in a shorter time. The reaction rate can be accelerated by raising the temperature or by adding a higher proportion of catalyst, but it is evident that the simplest procedure is, in principle, to increase the temperature, and hence this was the procedure chosen. Therefore, it was decided to carry out a new set of experiments (Design II), mainly in order to explore the effect of temperature. Since in Design I it was found that a 10 °C temperature increase almost doubled the reaction rate, a first set of nine new experiments were conducted at 80 °C with the same values of the Cat factor as in Design I (except for the experiments at the axial points): 0.03:1, 0.06:1 and 0.09:1. The values of the Met factor were also the same, except for one variation: since in the experiments conducted in the Design I it was found that it was not possible to attain a 100% conversion on using the 3:1 methanol/oil molar ratio, it was decided to use a ratio slightly above the stoichiometric one (4:1) in this new set of experiments. Thus, the values of the Met factor were 4:1, 6:1 and 9:1.
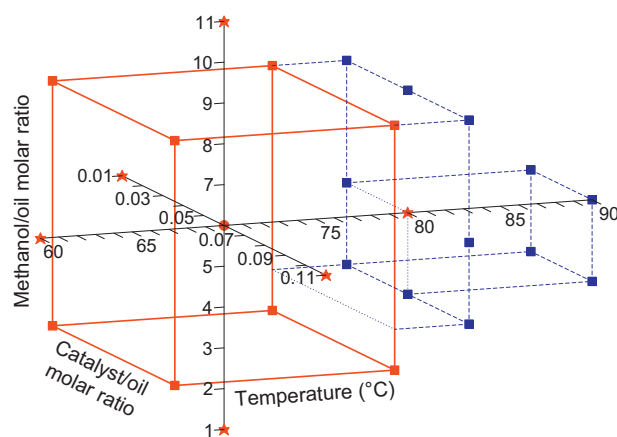
Fig. 2. Three-dimensional zone of the experimentation (Design I + Design II) showing the real values of the three factors whose influence on conversion was studied.

After these experiments at 80 °C, four new assays were conducted at 90 °C. Since in the experiments performed at 80 °C it was found that the Met factor was progressively less influential as the conversions attained became higher, the values of the Cat factor at this new temperature were 0.03:1 and 0.06:1, and the values of the Met factor 4:1 and 6:1. The operation conditions of the Design II experimental plan are shown in Table 2. With this new set of experiments, conversion was measured at six different reaction times in order to obtain the kinetic curves. The complete region of the values of the factors covered by this study is shown graphically in Fig. 2.

Finally, some experiments were carried out to determine the effect of the water and FFAs on the kinetics and on the conversion and additional experiments with a change of the scale of the reactor to check the reliability of the model were performed.

3. Results and discussion

3.1. Catalytic activity of DBSA

One of the advantages of using an acid catalyst in the synthesis of biodiesel from fats and/or oils is that the presence of FFAs in the reaction mixture does not lead to the formation of soaps or emulsions. The main disadvantage is that under mild reaction conditions transesterification with inorganic acid catalysts has a very slow reaction rate and hence this type of catalyst is not attractive from an economic point of view. However, the DBSA catalyst used here is not an inorganic acid and, unlike these, promotes a much faster triglyceride transesterification. Some kinetic curves of the
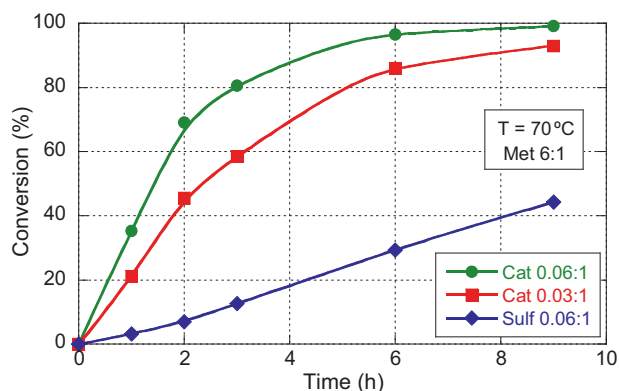
Fig. 3. Conversion of triglycerides vs. reaction time at 70 °C and Met = 6:1.

transesterification obtained using this catalyst as well as with sulfuric acid, both of them with a catalyst value of 0.06:1, are shown in Fig. 3. Fig. 3 also depicts a third kinetic curve, corresponding to a transesterification reaction performed with a Cat value of 0.03:1. The operation conditions for all the kinetic curves, shown in Fig. 3, were 70 °C and a Met value of 6:1. The conclusion drawn from this comparison is that DBSA has very high catalytic activity as compared to that of sulfuric acid, even when the Cat value used is only half the value of sulfuric acid/oil molar ratio (Sulf).

Several researchers have studied the acid catalysis of the transesterification of oils using sulfuric acid. Freedman et al. [25] studied the transesterification of soybean oil and sunflower oil with methanol at 65 °C with a Met value of 30:1 and 1% concentrated sulfuric acid based on the weight of the oil (Sulf ≈ 0.089:1). Despite the high Met values used, 69 h were required to attain high conversions (>95%, although that work does not specify the exact value of the conversion reached). Canakci and Van Gerpen [26] studied the transesterification of soybean oil at 60 °C with a Met value of 6:1 and a concentrated sulfuric acid/oil weight ratio of 0.01:1, obtaining a conversion of around 73% in 48 h. Upon increasing the Met value to 30:1 and the sulfuric acid/oil weight ratio to 0.03:1, the same authors attained a 98% conversion in the same reaction time. From the reports analyzed, it seems that when sulfuric acid is used as a catalyst, attaining a reduction in the reaction time requires the use of very high Met and Cat values. Thus, Zheng et al. [35] used canola oil as a raw material in transesterification reactions at 70 °C with a Met value of 245:1 and a Cat value of 3.8:1 to attain a conversion close to 100% in 4 h. All these results are in fairly good agreement with those obtained experimentally in this work using sulfuric acid as catalyst and they point to the superior performance of the DBSA as a catalyst in the transesterification of triglycerides.

3.2. Analysis of the results of Design I

The values of the factors and the responses of the first set of experiments carried out (a Rotatable Central Composite Design with five center points and six axial points, with a total of 19 experiments, designated Design I), are shown in Table 1. In order to analyze the effect of the values of the factors on the response, the conversions of triglycerides were determined at three different reaction times. However, of these three values for the response, only the conversion at 3 h of reaction was chosen for the analysis of the effect of the factors, because it was noted in most experiments that at 6 h of reaction time conversion was almost complete. It must be taken into account that the effect of varying the values of the factors at very high conversion levels is not significant because the differences in the values of the response lie within the order of random variations. Neither did we analyze the results for conversion at 1 h of reaction because, for very short reaction times (low

conversions), it was considered highly probable that the results would be influenced by the different kinetic mechanisms occurring during the early steps of the reaction due to the initial lack of miscibility of the reactants. In contrast, at 3 h of reaction, it can be considered that a complete miscibility of the reactants has already been reached in all experiments and, furthermore, that most of the experiments have not yet reached their reaction equilibrium.

3.2.1. Fitting of a response surface model to the conversion

After applying an ANOVA (see Section S1 in Supplementary content) to the experimental results (experiments 1–13 in Table 1) to determine the statistical significance of the influence of the factors, of their interactions, and of the existence of curvature, it was found that the curvature of the effect of the factors on the response was significant. Taking this into account, the prediction of the values of the response requires at least the use of a quadratic model. It was therefore considered convenient to carry out new experiments at the six axial points (Table 1, experiments 14–19) of the 2^3 full experimental design because in this way the new data obtained should help to calculate a better model, able to predict the values of the response with good accuracy even in zones close to the border of the experimental three-dimensional region (Fig. 2) of the values of the factors covered in this research.

In a first attempt, a model containing the quadratic terms of each factor and all the two-factor interactions was fitted to the results of the 19 experiments using the multiple linear regression technique. Thus, on comparing the values of the response predicted by the calculated model and the experimental values of the response, it was found that in the case of experiments 17 and 18 the residuals were too large. Next, upon scrutiny of these experiments it was noted that since in experiment 18 a proportion of methanol lower than the stoichiometric one had been used, it was logical that the result obtained would not follow the pattern found for the rest of the experiments, because it is highly likely that under those experimental conditions methanol would have been depleted at some moment of reaction and that the reaction had stopped. In fact, in the case of experiment 18 conversion only reached about 50% and remained steady at that value. Likewise, in experiment 17, the Cat value used was that of the upper axial point of the design. The finding that the results of this experiment did not fit the model may be understood taking into account that it was an experiment carried at the edge of the experimental region; that is, in the zone where any empirical model generates more inaccuracy due to its curvature. Consequently, this model was rejected and, for simplicity, the results of the analysis including all experiments are not shown.

In light of the above, it was decided that experiments 17 and 18 should be eliminated from the analysis and a new analysis by multiple linear regression should be applied to the seventeen remaining experiments, affording the model given by Eq. (3):

$$\widehat{X}_{3h} = 81.87 + 10.52 \times T + 18.28 \times Cat - 7.20 \times Met$$
$$- 1.15 \times T^2 - 15.70 \times Cat^2 +$$
$$2.91 \times Met^2 - 4.15 \times T \times Cat + 5.18 \times T \times Met \quad (3)$$
$$+ 3.97 \times Cat \times Met$$

In this model, $\widehat{X}_{3h}$ denotes the predicted value of the conversion at 3 h of reaction, and T, Cat and Met are the coded values of the factors. This model contains the linear terms of each factor and all the two-factor interactions. The remaining terms are the coded quadratic terms of the three factors, which are responsible for the curvature of the model. The coded and real values of each factor are given in Table 1, where it may be seen that a coded value of any factor equal to zero does not correspond to a null real value of this factor, but instead to the central real value of the range of values studied for that factor.

The model given by Eq. (3) can also be expressed in terms of the real values of the factors, as shown in Eq. (4):

$$\widehat{X}_{3h} = -231.61 + 5.90 \times T + 4055.05 \times Cat - 29.05 \times Met$$
$$-0.03 \times T^2 - 17,466.4 \times Cat^2 +$$
$$0.32 \times Met^2 - 23.06 \times T \times Cat + 0.29 \times T \times Met \qquad (4)$$
$$+44.09 \times Cat \times Met$$

Regarding Eq. (4), the negative value of the independent term can be explained in terms of the notion that this model is a curved empirical model and is therefore only valid in the region investigated, and that it does not make sense to calculate the value of the response for real values of the factors equal to zero.

It also seems appropriate to point out that although the model can predict – for some values of the factors – conversions higher than 100%, it should be understood again that this is a statistical empirical model with a curvature that is not asymptotic to 100% conversion and whose capacity of prediction is limited to the inner region within the experimental range of values of the factors.

Accordingly, the next step was to apply ANOVA to the regression model given by Eq. (3) to check the adequacy of the model. The results of the ANOVA (see Section S2 in the Supplementary content) indicate that the model represented by Eq. (3) is appropriate from the statistical point of view and can be used to predict the values of the conversion at 3 h of reaction, within the range of values of the factors studied.

3.2.1.1. Reliability of the model. The model given by Eq. (3) is an empirical model, and empirical models should only be used to predict conversions for values of the operating conditions within the range of experimentation. However, this transesterification reaction does not contain solid catalysts involving diffusion processes in pores and neither does the stirring rate have any significant influence on the kinetics of the transesterificación once the initial stages of immiscibility between reagents have been surpassed. Consequently, speculating that the model might be valid under experimentation conditions different from those used for its calculation, we performed some additional experiments to test its usefulness.

Thus, we carried out three experiments, holding constant the values of the three factors, Cat = 0.06, $T = 70\,^\circ$C and Met = 6, in three reactors of different shapes and sizes (we varied the size in three orders of magnitude): (a) closed cylindrical reactor, batch type, with 4 mL of reaction mixture; (b) closed, Erlenmeyer type reactor, with 40 mL of reaction mixture; (c) closed cylindrical reactor, with 400 mL of reaction mixture.

The result was that the experimental conversion obtained for the three reactors of different size and shape ($X_{3h;4mL} = 82.4$; $X_{3h;40mL} = 81.3$; $X_{3h;400mL} = 82.1$) agreed very well with that predicted by the model given by Eq. (3) ($\widehat{X}_{3h} = 81.9$).

In view of these results, it can be concluded that the model obtained for 3 h of reaction is useful for itself and it can be used to predict a wide range of conversions of triglycerides (from 50 to 96%) in a batch reactor, regardless of its shape and volume (at least 4 mL and 400 mL) provided it is well stirred.

3.2.2. Discussion of the effects of the factors on the response

The model represented by Eq. (3) indicates that the influence of the three factors on conversion is very complex because in the model there are linear, quadratic and, even, interaction terms of each factor.

On way to perceive the effect of the factors is by plotting the conversion of triglycerides against the values of the factors on contour plots. In Fig. 4, which was generated from Eq. (4) in order to use the real values of the factors, it can be seen that the influence of

both the T and Cat factors is not linear and positive; i.e., an increase in the values of these factors causes an increase in conversion. By contrast, the influence of the Met factor is non-linear and negative; an increase in the value of this factor results in a decrease in conversion after 3 h of reaction.

In the following sections, the influence of each of the factors and of their interactions on the conversion is discussed, taking into account the quantitative values and signs of each of the terms in Eq. (3).

3.2.2.1. Effect of temperature. Temperature is the second factor, after the Cat factor, with the most important influence on the response. The values of the regression coefficients in the model given by Eq. (3) provide a measurement of the relative influence of each of the factors and of their interactions on the response value. With respect to the influence of the T factor on conversion, it can be observed in Eq. (3) that there are linear, quadratic and interaction terms in which this factor is involved that contribute to this influence. Accordingly, although in principle the effect of the T factor can be positive at low values of the T factor due to the influence of the linear term containing the temperature factor in Eq. (3), an increase in temperature will not always entail an increase in conversion. In fact, as the value of T increases, the value of the negative quadratic term will become progressively higher, cancelling or even overcoming the influence of the positive linear term at sufficiently high temperatures. The curved influence of temperature on conversion can be recognized in the contour plots shown in Fig. 4, especially at high temperatures.

Furthermore, the quantitative effect of the T factor for each experimental condition was calculated from Eq. (5), which is the partial derivative of Eq. (3) with respect to temperature. The results are collected in Table S3 in the Supplementary content and the evolution of the effect of temperature on conversion vs. temperature is plotted in Fig. 5a.

$$\frac{\partial X_{3h}}{\partial T} = 10.52 - 2 \times 1.15 \times T - 4.15 \times Cat + 5.18 \times Met \qquad (5)$$

From Eq. (5), and mainly from Fig. 5a, it can be seen that the influence of the T factor on conversion is positive at 3 h of reaction; the higher the temperature, the higher the conversion. However, this positive effect becomes progressively smaller as temperature increases. This a logical result since at the higher values of the T factor of the experimental zone studied conversion is close to 100%, which is its theoretical and experimental limit, and the model was calculated only from the experimental results. The explanation is that the effect of any factor at conversions close to 100% should be close to zero, except when the backwards reaction of the equilibrium is important, and this circumstance was not observed in this work.

Furthermore, it is important to note that the observed effect is limited to the range of the T factor values studied in the Design I experimental plan (Table 1).

The increase in conversion with temperature is due to the strong effect of temperature on the reaction rate constant, in accordance with the Arrhenius equation. Any increase in temperature increases the value of the kinetic coefficient and therefore the reaction rate, leading to a higher conversion in a given time. Another possible influence is that an increase in temperature produces a decrease in viscosity, favoring the miscibility of the reactants and hence the reaction rate.

This effect is different from that reported by other authors for the transesterification of sunflower oil and methanol with a basic catalyst [33,34]. In these studies, the influence of temperature was negative; that is, an increase in temperature decreased the conversion because the saponification reaction, which is an unwanted side reaction, began to become important. Only in cases where very
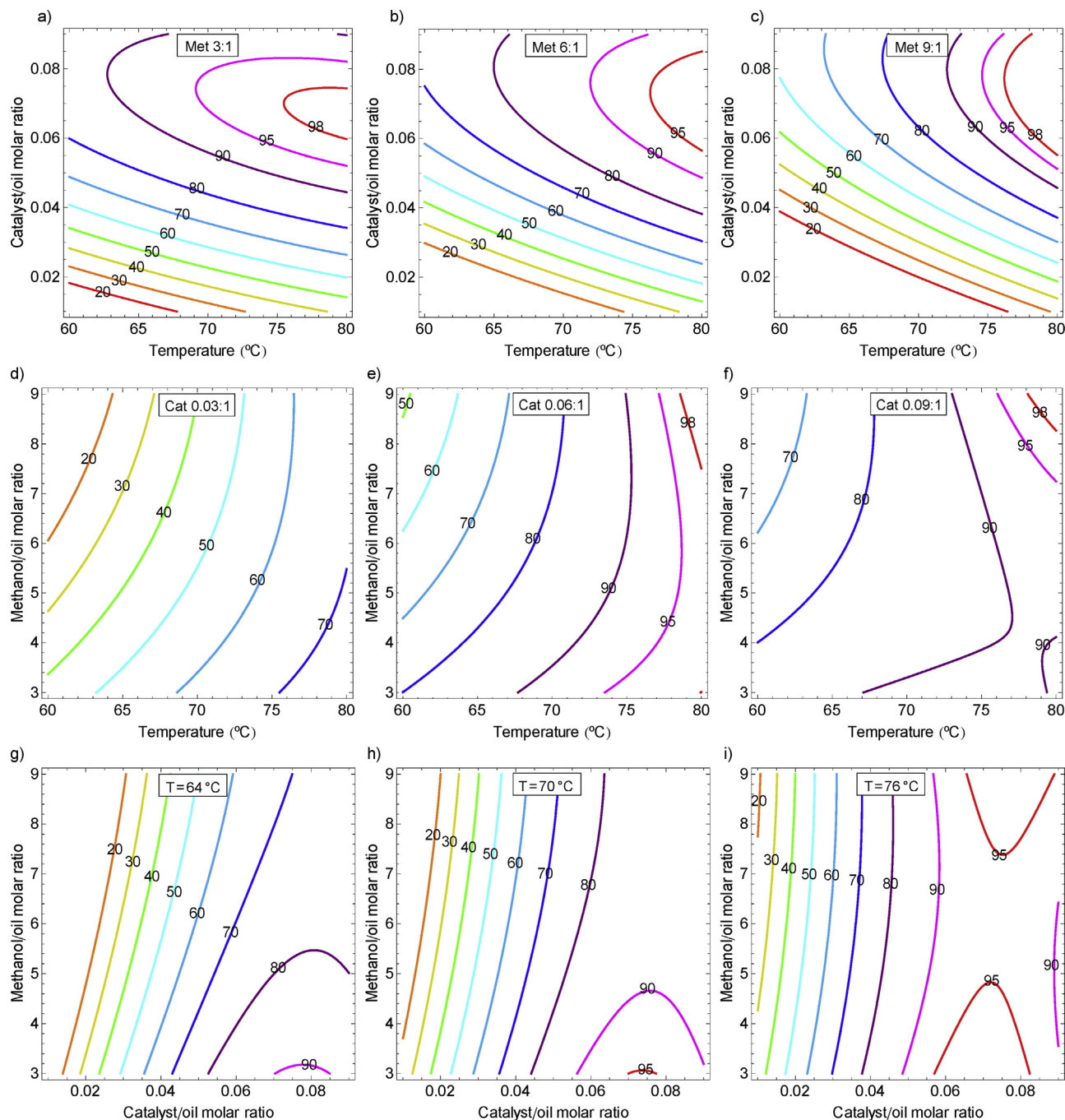
Fig. 4. Contour plots showing the conversion values at 3 h of reaction calculated from Eq. (4) as a function of the values of two of the factors, holding the value of the third factor constant.

low temperatures (20–32 °C) were used did a positive influence of temperature on the conversion of high-oleic sunflower oil appear [36].

The advantage of the acid catalyst used in the present work is that it does not produce saponification reactions and that within the experimental temperature range the temperature effect is always positive. In other words, there is no clear evidence that the backward reaction (transesterification is a reversible reaction) limits the progress of the reaction until completion. The effect of temperature found in this work for the DBSA does match the results concerning other acid catalysts for a temperature range similar to the one used in this work [26,35]. Nevertheless, Yingying et al. [37], using sulfuric acid as catalyst, found that at 165 °C an increase in temperature was

not beneficial to the kinetics, although the reason for this different effect may be that at high temperatures, the miscibility of biodiesel and glycerol is higher and the backward reaction begins to become important.

3.2.2.2. Effect of catalyst. The Cat factor has the strongest influence on the conversion. As shown in Eq. (3), the influence of this factor is complex, as in the case of temperature, since in Eq. (3) there are terms containing the coded value of this factor with positive and negative signs and, also, interaction terms. Positive terms indicate that conversion increases when the values of the Cat factor increase, and terms with negative signs indicate the opposite; that is, that conversion increases when the values of the Cat factor
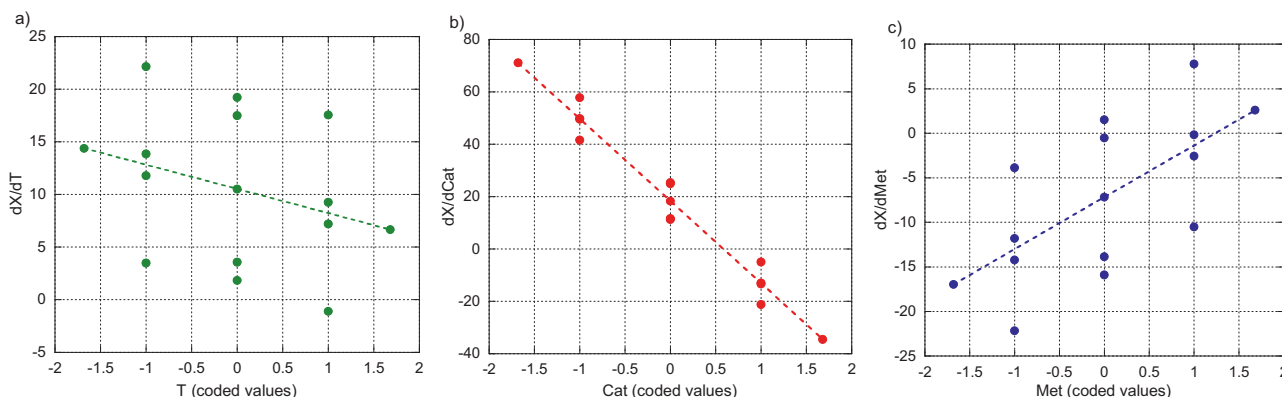
Fig. 5. (a) Variation of the effect of the T factor on conversion at 3 h of reaction time as a function of the value of the T factor. (b) Variation of the effect of the Cat factor on conversion as a function of the value of the Cat factor. (c) Variation of the effect of the Met factor on conversion as a function of the value of the Met factor.

decrease. Moreover, the existence in Eq. (3) of a quadratic term of the Cat factor and of an interaction with a negative sign indicates that upon increasing the values of the Cat factor the value of this quadratic term may exceed the value of the terms with positive sign. The consequence is that the overall influence of the Cat factor on conversion can become negative.

The curved influence of the proportion of catalyst on conversion can be seen in the contour plots shown in Fig. 4, especially at high values of the Cat factor. As in the case of temperature, the quantitative value of the effect of this factor in each experiment was calculated using Eq. (6). The results are collected in Table S3 in the Supplementary content. The evolution of this effect *vs.* the values of the Cat factor are plotted in Fig. 5b, where it can be observed that the effect becomes negative at high values of the Cat factor, i.e., at high conversions.

$$\frac{\partial X_{3h}}{\partial Cat} = 18.28 - 2 \times 15.7 \times Cat - 4.15 \times T + 3.97 \times Met \qquad (6)$$

The increase in conversion as the values of Cat factor are increased can easily be explained if it is considered that the catalyst decreases the activation energy of the reaction, in accordance with the Arrhenius equation, by providing an alternative mechanism for the progress of the reaction through the formation of intermediate compounds between the reactants and catalyst. Accordingly, the higher the Cat values the higher the formation rate of the intermediates, and the greater amount of these. Furthermore, the cancellation of the effect of the catalyst on conversion at high values of the Cat factor (high conversions) can be attributed to the fact that the model should satisfy the condition that when conversion is about 100% (its theoretical and practical limit) the overall effect of all the factors must approach zero. The finding that the effect passes from being positive to negative suggests that within the range of values of the Cat factor in which the experimentation was performed there is an optimal value of the Cat factor.

As was the case with temperature, the effect of the Cat factor is opposite to that found by other authors using basic catalysis [33,34]. The explanation given by the authors in those works is that an increase in the values of the Cat factor reduces conversion because it facilitates the saponification reaction. However, since with acid catalysis there is no possibility of soap formation, this problem does not arise in our case.

The common conclusion regarding temperature and catalyst on conversion is that their effect is positive for low conversions and that their global effect is progressively annulled, or even changes its sign, when conversion approaches 100%.

3.2.2.3. Effect of methanol. According to Eq. (3), the influence of the Met factor on conversion is curved; at low values of the Met

factor the influence of this factor is negative, but when the values of the Met factor increase the value of the quadratic term, which has a positive sign, counteracts the primary negative influence of the linear term on conversion. Besides this, the Met factor also influences the value of conversion through the effects of its interactions with other factors. From the contour plots in Fig. 4 it can be deduced that the influence of methanol is higher at the lower values of the T and/or Cat factors, which correspond to low triglyceride conversions. Moreover, the global quantitative effect of the Met factor in conversion was calculated with Eq. (7). The values of the effects are collected in Table S3 in the Supplementary content and the evolution of this effect *vs.* the values of the Met factor is plotted in Fig. 5c, where it can be seen that the higher the values of the Met factor, the less negative the effect, this becoming slightly positive at very high values of this factor, but only in the case in which the conversions are >80%.

$$\frac{\partial X_{3h}}{\partial Met} = 7.20 + 2 \times 2.91 \times Met + 5.81 \times T + 3.97 \times Cat \qquad (7)$$

The explanation for these observations is not clear, since in principle it could be speculated that an increase in the value of the Met factor should increase the reaction rate due to the increase in concentration of one of the reactants. However, it should be noted that at the beginning of the reaction the reaction mixture is biphasic and the reaction takes place in the oily phase or at the oil–methanol interface, and also that the concentration of methanol in the oily phase is determined by the solubility of methanol in the oil. In this situation, the oily phase is always saturated by alcohol, such that an excess of methanol does not involve an increase in its concentration in the oily phase and, as a consequence, no increase in the reaction rate occurs. In fact, a higher value of the Met factor in the reaction mixture leads to more oil and catalyst remaining in the methanolic phase and thus becoming unavailable for reaction in the oily phase, which is where the reaction apparently occurs. The result is a decrease in the reaction rate. This effect is more important at lower conversions because with increasing conversion miscibility is improved and more methanol is available in the oily phase.

This effect is opposite that obtained for the transesterification reactions that occur in the alcoholic phase, via either acid or basic catalysis. In these cases, because of the low solubility of the oil in alcohol, higher values of the Met factor are advantageous because there is a larger amount of oil available for reaction in the alcoholic phase. However, there are differences between acid and basic catalysis. In basic catalysis, the influence of the Met factor is positive, although practically negligible [33,34], and the best results are obtained with ratios of 6:1 and 9:1 [23–25]. Above these values, no significant improvements are found, probably due to the effect of dilution of all the reactants. Regarding this, the reaction time at

which the effects are measured must also be taken into account because since basic catalysis is very fast the immediate formation of biodiesel favors complete miscibility of the reactants, and when they are fully miscible the increase in the reaction rate due to the increase in the proportion of one of the reactants can be counteracted by the decrease in the concentrations of the other reactant and catalyst. In acid catalysis with sulfuric acid, however, the slowness of the reaction causes a longer period of phase immiscibility and hence an increase in the value of Met favors the miscibility of a greater amount of oil in the alcohol phase, which is where the reaction occurs. Thus, the optimum ratio was found to be approximately 30:1 [26,37]. However, the possibility that the excess alcohol might help to displace the reaction equilibrium to the right should not be overlooked, and this is an important factor if high conversions are to be achieved.

3.2.2.4. Effect of the temperature–catalyst interaction. The effect of an interaction is a change in the value of the effect of a factor on the response when the value of a second factor undergoes a variation.

According to the model given by Eq. (3), the effect of the T–Cat interaction is significant and has a negative influence on the response. This means that the influence of the T factor is stronger for the lowest Cat values, i.e., the increase in the conversion due to an increase in the T factor increases as the Cat values decrease. Similarly, the influence of the catalyst is greater at low temperatures; increasing the values of Cat increases conversion and this increase is greater in the case of the lower values of the T factor.

The reason for this behavior has been discussed previously. First, the response measured is the conversion of triglycerides at a given reaction time and this conversion increases rapidly with increases in the T and/or Cat factor values. Second, at high conversions the effect on conversion of varying any factor must decrease gradually until it becomes null at 100% conversion, except in the case in which the reverse reaction is significant. Accordingly, the effect of any significant factor will be higher as conversion decreases and, therefore, a variation in the values of the T or Cat factors has a greater influence on the response when the value of the other factor is lowest.

The conclusion from the effects of T, Cat and the T–Cat interaction is that high conversions can be attained by increasing the level of any of these factors and that it is not necessary for the two factors to have high values. Thus, the decision as to whether to use higher values of the T factor or higher values of the Cat factor in the process requires a study of the economic optimization of the entire process.

3.2.2.5. Effect of the temperature–methanol interaction. The T–Met interaction is positive. This means that the increase in conversion caused by an increase in T is higher for the high value of the Met factor, and since the effect of Met is negative this interaction implies that the decrease in conversion due to an increase in the value of Met is lower for the high value of the T factor (Fig. 4d–f).

3.2.2.6. Effect of the catalyst–methanol interaction. The Cat–Met interaction is positive but less so than in the case of the T–Met interaction. This means that the higher the Met value, the larger the influence of a change in the Cat value on the response value. Similarly, the larger the Cat value, the lower the effect of methanol, i.e., since the effect of methanol is negative, this interaction means that the decrease in conversion due to an increase in the Met value is lower for high Cat values.

From these results, it is possible to draw the following conclusions with respect to methanol. Methanol is an obstacle at low conversions because it slows down the reaction. However, under high temperatures and/or high proportions of catalyst, (i.e., for conversions >80%), after the problem of the miscibility of the reactants has been circumvented, methanol favors higher conversions by

shifting the equilibrium to the right in the reversible transesterification reaction.

3.2.3. Optimization

From the results obtained in the experiments performed in the Design I experimental plan, it can be seen that under certain experimental conditions it is possible to obtain conversions close to 100%. In Fig. 4a it can be seen that the highest conversions are obtained at temperatures close to 80 °C. Furthermore, an optimization was carried out to find the optimal operating conditions; i.e., the optimum values of the factors at which the maximum response value is obtained. Thus, on performing a mathematical optimization of the model given by Eq. (4) within the range of the experimental conditions, the optimal values of the factors were T = 80 °C, Cat = 0.0683, and Met = 4, all of them in real values (under these conditions, the model predicts a maximum conversion of 97.7%). However, among these conditions there is an extreme point (T = 80 °C) of the range of the experimental conditions where the accuracy of the predictions is not as good as for the innermost points of the experimental area. Therefore, the use of 76 °C as the best temperature condition seems more appropriate. At this temperature, Fig. 4i exhibits a saddle point, and above and below this point the region of experimental conditions under which it is possible to attain conversions higher than 95% can be found. From an economic point of view, a low Met value is preferred, and hence the upper region should be discarded and the lower region should be used. Therefore, the optimum values for the operating conditions will be those that result in a conversion higher than 95%, at a temperature of 76 °C, with the lowest Met value (Cat values between 0.06:1 and 0.08:1 and Met values below 5:1).

3.3. Results of the Design II experimental plan

In view of the results obtained in the Design I experimental plan, it was decided to carry out a new set of experiments, mainly in order to explore the effect of temperature on the kinetics of the reaction. The experimental conditions of this new set of experiments (Design II) are given in Table 2.

The results of the experiments performed in Design II are shown graphically in Fig. 6.

3.3.1. Discussion of the kinetic curves
3.3.1.1. Effect of the Cat factor on the kinetic curves. Fig. 6a–c, shows the strong effect of the change in the value of the Cat factor on the kinetics of transesterification at 80 °C.

The explanation for this result is similar to that given earlier in this work. In Fig. 6a–c, it is clear that for low conversions the effect is very strong but that this effect vanishes when conversion approaches 100%. Fig. 6d also shows that in the case of the reaction carried out at 90 °C the effect of a change in the value of the Cat factor on conversion decreases as conversion increases. The explanation for this is the same as above: the higher the conversion, the lower the effect of the Cat factor on conversion due to the proximity of conversion to 100%; that is, a point at which none of the factors can have any effect, unless the reverse reaction is important.

3.3.1.2. Effect of the Met factor on the kinetic curves. The effect of methanol is the same as that described in previous sections of this work. At low conversions, it is possible to see a certain negative influence of the Met factor: the higher the value of the Met factor, the lower the reaction rate. However, this negative effect vanishes as conversion becomes higher. The effect of methanol is more difficult to appreciate in the case of 90 °C (Fig. 6d) because it is almost null. At higher temperatures, the unfavorable effect of the immiscibility of the reactants on the reaction rate almost disappears and,
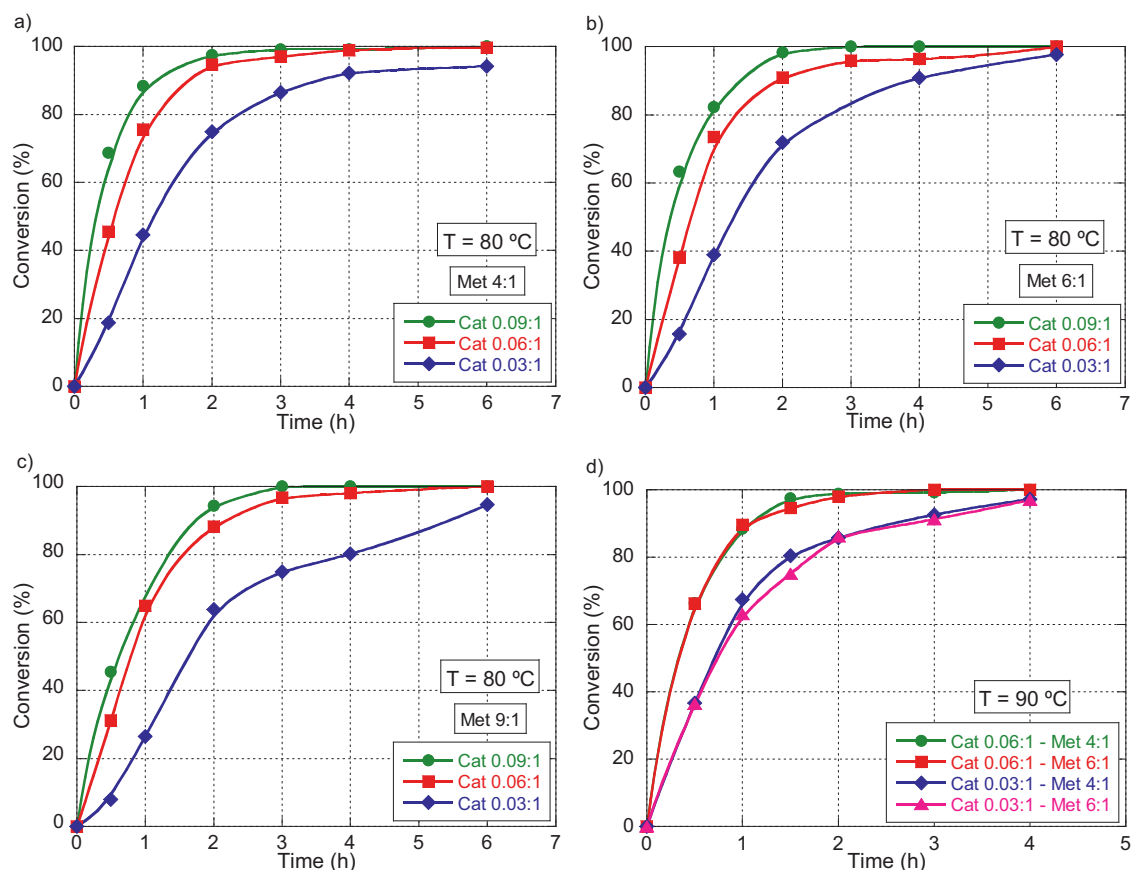
Fig. 6. Kinetics of the transesterification reaction at the values of the *T*, Cat and Met factors of the Design II experimental plan. The values of the factors at which the experiments were performed are given in each plot.
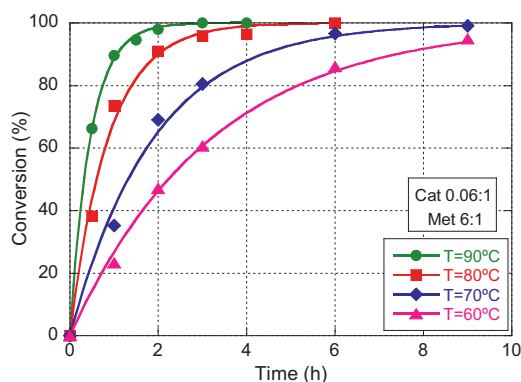
Fig. 7. Kinetics of transesterification at 60–90 °C, with Cat = 0.06:1 and Met = 6:1 Symbols represent the experimental data and solid lines represent the prediction of the model (Eq. (8)).

consequently, conversion rises very rapidly; very high conversions being obtained even with values of Met as low as 4:1.

3.3.1.3. Effect of the T factor on the kinetic curves. Fig. 7 shows the transesterification kinetics at four different temperatures, holding the proportions of catalyst and methanol constant. These plots include the experimental data from the Design I and the Design II experimental plans.

The influence of temperature is evident and it can be observed that an increase of 10 °C almost doubles the reaction rate at low conversions. This effect is similar to the results reported by Zheng

et al. [35] who, using sulfuric acid as catalyst, found that an increase in temperature from 70 to 80 °C almost doubled the reaction rate.

The first conclusion that can be drawn from Fig. 7 is that the effect of temperature on conversion decreases with increasing conversion. The reason for this has been reported in previous sections of this paper. The second conclusion is that these kinetic curves seem to be suitable to attempt a modeling of the kinetics of the transesterification reaction. In this respect, it is known that the mechanism of the transesterification reaction is complex because several simultaneous and consecutive reactions may occur, this implying that the number of parameters of the resulting model would be high and, consequently, that the result of the calculation of these parameters would result in a large uncertainty. Consequently, a more practical alternative is to adjust a simplified model to the data, because if this model allowed the prediction of conversion in different reaction conditions with sufficient accuracy its use would be feasible in design tasks.

Following this idea, a pseudo-first order model was fitted to the kinetic data shown in Fig. 7. In a batch reactor, the conversion for a reaction between liquid reactants with first-order kinetics can be calculated by means of Eq. (8):

$$X_A = 100 \times [1 - \exp(-k \times t)] \tag{8}$$

where X_A is the conversion, in %, of the triglycerides to biodiesel, at time t, and k is the effective kinetic coefficient in h^{-1}. The fitting of this model to the data of each of the four temperatures studied afforded the kinetic coefficients given in Table 3, where it can be observed from the values of the determination coefficients, R^2, that the model fits the experimental data surprisingly well.

Once the values of the effective kinetic coefficients for each of the four temperatures were calculated, it was possible to determine

Table 3
Effective kinetic coefficients and apparent activation energy for the transesterification of sunflower oil with DBSA as catalyst.

T (K)	k (h^{-1})	R^2	E_a (kJ/mol)
333	0.31	0.998	
343	0.53	0.993	66.3
353	1.15	0.992	
363	2.17	0.999	
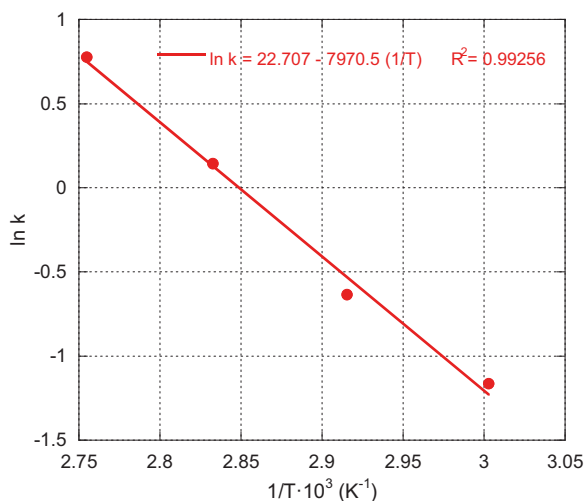
Fig. 8. Plot of ln k vs. 1/T for the transesterification of sunflower oil with DBSA as catalyst at 60–90 °C, with Cat = 0.06:1 and Met = 6:1.

the value of the apparent activation energy through the Arrhenius equation, in the form given by Eq. (9):

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (9)$$

where E_a is the apparent energy of activation of the reaction; R is the gas constant, T is the absolute temperature, and A is the preexponential factor.

According to Eq. (9), a plot of ln k vs. 1/T should give a straight line with a slope equal to $(-E_a/R)$ and this can be used to calculate the value of the apparent activation energy, E_a. This plot is shown in Fig. 8. The resulting apparent activation energy calculated from the value of the slope of the straight line was 66.3 kJ/mol.

Other authors have found similar values for the activation energy in transesterification reactions. For instance, Freedman et al. [38] found a value of 14.92 kcal/mol (62.4 kJ/mol) for the transesterification of soybean oil with 1 wt% H$_2$SO$_4$ at five temperatures, ranging from 77 to 117 °C.

The surprisingly good fit of the first-order kinetic model to the experimental conversions and the good fit of the Arrhenius equation to the data of the kinetic coefficients suggest that these good results are not accidental but are probably due to the fact that the slowest step (the controlling step of the global rate of the process) among the multiple reactions involved in the transesterification process is the reaction between the triglyceride and the catalyst to form an intermediate.

3.4. Effect of water and FFAs

Low-cost raw materials usually contain FFAs and small amounts of water, although considering that water and oil are insoluble, any amount of water above its solubility in the low-cost oil could be separated easily by decantation before beginning the transesterification process. However, water will also be formed as a byproduct in the esterification of the FFAs existing in this type of feedstock.
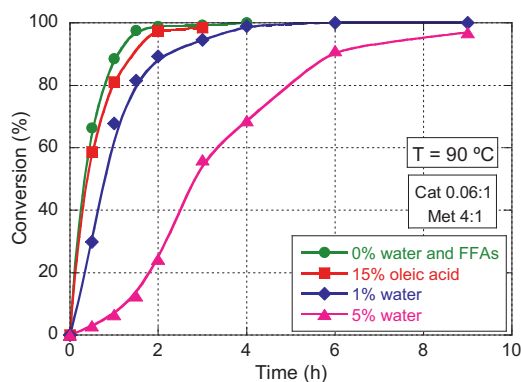
Fig. 9. Kinetics of the transesterification reaction of: ——●—— pure sunflower oil without water or FFAs, ——■—— oil with 15 vol% of oleic acid, ——◆—— oil with 1 vol% of water based on the volume of oil and ——▲—— oil with 5 vol% of water based on the volume of oil.

Therefore, when low-cost raw materials are used, the water in the reaction mixture will hydrolyze the biodiesel, producing FFAs, regardless of the type of catalyst used. The advantage of an acid catalyst is that no saponification reactions take place. Moreover, the most important advantage of the DBSA catalyst is that since the reaction takes place in the triglyceride phase and water prefers the methanolic phase, the kinetic effect of water will be small at the beginning of the reaction, while at the end of the reaction the effect of water will be almost null because it will strongly prefer the glycerol phase. Since in the biodiesel phase there will be much more methanol than water, the thermodynamic effect will also be small or null. Fig. 9 shows the results of experiments carried out to study the effect of water and FFAs on the reaction kinetics.

The curves in Fig. 9 show the decrease in reaction rate due to the presence of water, this decrease becoming more pronounced as the proportion of water rises. It can be seen that in the kinetics with 1 vol% water in oil, the decrease in the reaction rate is not very pronounced and a conversion close to 100% can be attained after 4 h. The kinetics with 5 vol% water is much slower but the reaction also attains a conversion close to 100% in the preset reaction time. The decrease in the reaction rate can be explained taking into account the hydrolysis of biodiesel, the decrease in the methanol concentration due to the presence of water and, mainly, the decrease in the catalyst concentration in the oil phase (the phase in which the transesterification reaction takes place). Water is more basic than methanol and favors ionization of the catalyst, increasing its concentration in the methanol phase [13]. Furthermore, although the hydrolysis reaction contributes to decreasing the net rate of biodiesel formation in the initial reaction stages, in both cases (1 and 5 vol% water) the reaction can attain conversions close to 100%. This suggests that water has practically no influence in the transesterification equilibrium due to its solubility in the glycerol phase.

Previous studies using acid catalysts (sulfuric acid and p-toluenesulfonic acid) have reported an apparently much important effect of water, but these results are not strictly comparable with those obtained here because they were performed at different temperatures and because they do not specify the time needed to reach conversions close to 100% [26,39].

The effect of the presence of FFAs (in this case, oleic acid) in the oil is even lower than that of water. The concentration of water produced by the esterification of oleic acid, at a ratio of 15 vol% in the oil, is about 1 vol%, such that in principle the kinetic behavior should be expected to be similar. However, the decrease in the reaction rate is much greater in the case of water being added initially, because in the case of water formation during the FFAs esterification, the water synthesized is transferred to the glycerol phase, which is formed in parallel to the synthesis of water.

The conclusion is that the presence of water and/or fatty acids in the oil slows down the transesterification reaction rate but does not prevent conversions close to 100% from being reached. In sum, since small water or FFAs proportions do not essentially alter the reaction course, low-cost oils are completely compatible with this catalyst without any special treatment and, in the same way, cheap technical grade methanol can also be used for the transesterification process.

3.5. Catalyst recovery and biodiesel purification

While separation of the catalyst from biodiesel is necessary to meet ASTM D6751 regulations, the convenience for recovery and reuse of the catalyst depends on the economics of the process. Thus, from the economic point of view, its recovery for reuse does not appear to be very important given the cost of this catalyst. The DBSA catalyst is a compound that is massively used in the manufacture of detergents and can be acquired in barrels of 200 kg at a price of around €2/kg. According to this price, in a biodiesel synthesis with a catalyst/oil molar ratio of 0.06/1, about 18 g of catalyst per liter of biodiesel produced are used. This represents an additional cost of only about €0.036/L. According to these data, it is very likely that the recovery of the catalyst, for the sole purpose of its reuse, would not be profitable.

However, the separation of the catalyst from the biodiesel is important to achieve the degree of biodiesel purity required for its commercial use. This separation can be accomplished by any of the methods described below.

A procedure that we have already used in a previous study [13], although with a more hydrophobic catalyst than the one used in this work, consists of the following steps:

(a) Separation of glycerol by decantation.
(b) Separation of methanol by evaporation.
(c) Separation of the biodiesel–catalyst mixture by passing it through a column packed with silica gel particles in which the catalyst is able to protonate the silica gel in a reversible manner. The loss of the catalyst proton produces a highly polar species which is not eluted with the biodiesel or any other non-polar solvents.
(d) Once all the biodiesel has come out of the column, the catalyst is eluted from the column by using a flow of methanol that activates the acid-base equilibrium, and the active catalyst, in its sulfonic acid form, can be recovered from the column, without no apparent loss of activity.

Although this approach allows the separation of all the reaction mixture components, in a search for a simpler and more efficient procedure we have explored alternative routes. Specifically, we have conducted preliminary tests with a procedure involving the following steps: neutralization of the catalyst in the reaction mixture with sodium or calcium carbonates; evaporation of methanol; glycerol separation by decantation; and washing of the biodiesel phase, at least twice, with water.

The biodiesel obtained after this procedure showed the following characteristics:

(1) Biodiesel calcination afforded no solid waste.
(2) Biodiesel acidity was tested by the standard procedure (UNE-EN 14104) and was in full agreement with the regulations (UNE-EN 14214 and ASTM D6751).
(3) The absence of glycerides and catalyst was checked by ^{1}H NMR and chromatographic methods. In the Supplementary content (Section S4) the results of ^{1}H NMR, GC–MS and HPLC–MS analyses can be found.

Once the biodiesel has been separated by this procedure, it must be taken into account that the catalyst remains in the glycerol phase. The separation of the catalyst from the glycerol is important because the commercial value of the glycerol can be increased, although in this case, as in previous cases, the importance of the purification depends on the economics of the process.

The traditional route for the purification of glycerol is distillation. With this procedure the glycerol distills and the solid catalyst salt remains as a residue. This salt can be regenerated to its acid form by ion exchange procedures. However, we are currently also studying the way to separate the catalyst from the glycerol using procedures based on adsorption of the catalyst in its ionic or acid form on sorbents of different types: hydrophobic, hydrophilic, and ion exchange resins.

The conclusion is that there are many promising ways to recover the catalyst and/or to purify the reaction products, but this research requires detailed systematic work based on economic criteria, now ongoing.

4. Conclusions

The synthesis of biodiesel from triglycerides and methanol using 4-dodecylbenzenesulfonic acid as catalyst was studied. First, a set of experiments was carried out to determine the effect of three factors on triglyceride conversion: temperature and the catalyst/oil and methanol/oil molar ratios. Next, in another set of experiments the variations in the reaction kinetics with temperature were studied. From this study the following conclusions can be drawn.

The rate of transesterification obtained with this catalyst is much higher than that achieved with sulfuric acid. In this respect, at temperatures below 80 °C the use of this catalyst allows conversions close to 100% to be achieved in less than 3 h upon using a catalyst/oil molar ratio of 0.068 and a methanol/oil molar ratio as low as 4. In contrast, when sulfuric acid is used as the catalyst, the use of values of methanol/oil molar ratios higher than 30 is usual.

From the results of the first set of experiments, and using multiple linear regression, we calculated an empirical model that relates the value of conversion, at 3 h of reaction, and the values of the influencing factors quantitatively. From this model it is possible to determine the effect of the factors on conversion. The conclusion from the effects of temperature, of the catalyst and of their interaction is that high conversions are attained by increasing the level of any of these factors and that it is not necessary for both factors to have high values. Since with this catalyst no saponification reactions are produced, as in the case of alkaline catalysts, no an optimal value for the reaction temperature was found. Consequently, the decision about whether to use higher temperatures or higher proportions of catalyst in the process requires a study of the economic optimization of the entire process.

Regarding the effect of methanol, it is possible to draw the following conclusion: methanol is an obstacle at low conversions because it slows the reaction down. However, at high temperature and/or high proportions of catalyst (i.e., for conversions >80%), after the problem of the miscibility of the reactants has been overcome, methanol favors higher conversions by shifting the equilibrium of the reversible transesterification reaction to the right.

Moreover, from the model obtained, the contour plots of the effects of the factors on conversion were determined. From these plots it is possible to find the best experimental conditions to achieve conversions higher than 95%.

A second set of experiments performed at 80 and 90 °C was also carried out. From the analysis of the results of all the experiments performed in this work, in which the values of the catalyst and methanol molar ratios were held constant, it was found that the transesterification kinetics behaved as a pseudo first-order

reaction, with activation energy of 66.3 kJ/mol. At 90° C it was possible to obtain conversions higher than 98% in less than 2 h.

Experiments conducted to determine the effect on conversion of the presence of water and FFAs in the reaction mixture showed that FFAs (15 vol% of oleic acid in oil) and small amounts of water (≤1 vol% of water in oil) had no significant effect on either the kinetics or on reaction equilibrium and that higher amounts of water may slow down the reaction kinetics but do not prevent conversions close to 100% from being achieved due to the high solubility of water in the glycerol phase.

Taking into account that the catalyst used is a readily available commercial product, its use should provide a more economical way of performing transesterification reactions from inedible feedstock.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2014.06.033.

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